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⑧ **Transparent aqueous tin compound solution and method of producing transparent conductive tin oxide.**

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AU-A- 513 419
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CHEMICAL ABSTRACTS, vol. 99, no. 20, 1983,
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US; & SU-A-1 033 440 (V.P. KARLOV et al.)
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Description

Background of the Invention

a) Field of the Invention

5 This invention relates to a transparent aqueous tin compound solution suitable for forming transparent conductive tin oxide and to a method of producing transparent conductive tin oxide using said aqueous solution.

b) Description of the Prior Art

10 In recent years, accompanied with the remarkable development in the field of electro-optical elements, attention is paid to transparent conductive membranes of the type of SnO_2 or In_2O_3 . They are actively developed, for example, as transparent electrodes of various optical devices such as those of electroluminescence, liquid crystals, image accumulation devices, etc.; as heating elements or resistors utilizing their heat resistance and anti-abrasion properties; as solar cells utilizing their high conductivity; or as selective permeable membranes for use in solar heat electricity generation utilizing their high reflexivity in infrared.

Among the methods of forming these transparent conductive membranes are known:

(1) chemical vapor deposition method.

(2) vacuum evaporation method.

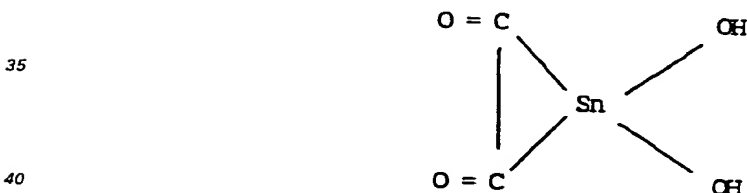
20 (3) sputtering method.

(4) coating method.

All of the above-mentioned methods (1)—(3) use complicated apparatus and are inferior in operability. In addition, they usually necessitate an etching step after membrane formation, to form a pattern.

In the method (4) also, when using an inorganic salt such as SnCl_4 for example, since hydrogen chloride or other chloride gases are generated upon heat decomposition, severe corrosion of the apparatus takes place. Also, the chlorine remaining in the membrane may become a cause of impairing the conductivity. There are also methods of using organic acid salts such as octyl acid tin salt or an organic complex. But in these methods, there are problems such that the uniformity of the membrane is impaired upon heat decomposition or gelation of the coating liquid takes place. Moreover, they have defects such that the formed membrane is uneven, cloudy and is liable to get hurt.

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is produced by reacting tin (II) oxalate with hydrogen peroxide in a 1:1 molar ratio. However, the tin oxide obtained by the use of this product is of extremely low electrical conductivity.

45 We, the inventors, taking the above-mentioned problems of the prior art into account, carried on further studies, and as a result, we attained this invention.

The object of this invention is to provide a transparent aqueous tin compound solution which has no restriction or problem on the apparatus, has high applicability, and can finally form tin oxide having excellent transparency, uniformity, compactness and conductivity, in an industrially advantageous manner, and to provide a method of producing transparent conductive tin oxide by using said aqueous solution.

Summary of the Invention

55 The above-mentioned object of this invention is attained by a transparent aqueous tin compound solution formed by reacting a tin carboxylate with hydrogen peroxide in molar ratio of 1:1.5 or above, in an aqueous medium, and by calcinating said aqueous solution at a temperature above 400°C .

Detailed Description of the Invention

60 As the tin carboxylates used in this invention may be mentioned for example, stannous formate, stannous acetate, stannous oxalate, stannous tartrate, etc. However, for the attainment of this invention, stannous oxalate is preferable.

The quantity of hydrogen peroxide should be 1.5 mol or more, preferably within the range of from 1.6 to 2.2 mol for one mol of the tin salt. When the quantity goes beyond the lower limit of the range, the compactness and conductivity of the finally obtained tin oxide will be lowered, and also no improvement in performance will be observed even if it is used in a quantity more than the actual necessity.

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As the aqueous medium, water is usually used, but an amount of a water-miscible organic solvent may be used together in a range in which a viscosity rise or gelation of the reaction-produced solution will not occur.

5 The method of producing the aqueous solution of the object is to add a tin carboxylate to an aqueous medium under stirring and then add a prescribed quantity of hydrogen peroxide.

Even if the reaction is initiated at room temperature, there are cases where boiling may take place by the reaction heat. Therefore, when the reaction is conducted at a temperature below the boiling point, it is desirable that the concentration of the tin carboxylate should be determined generally below 20 weight %, preferably below 18 weight %.

10 In order to provide a transparent aqueous solution in which a dopant is uniformly contained and which can finally form tin oxide having excellent transparency, uniformity, compactness, conductivity, etc., it is desirable to make a dopant coexist in the reaction system. Among such dopants may be mentioned compounds containing elements of Ib Group such as Cu, Ag, Au; those of IIIa Group such as Ce, Eu; those of Va Group such as V, Nb, Ta; those of Vb Group such as As, Sb, Bi; those of VIa Group such as Cr, Mo, W; 15 those of VIIa Group such as Re; those of VIII Group such as Ru, Rh, Pd, Os, Ir, Pt; and fluorine. Among others, compounds containing elements selected from Ib, Va, Vb, VIa, VIII Groups and fluorine are preferable. Especially, coexistence of antimony oxides such as Sb_2O_3 , Sb_2O_4 , Sb_6O_{13} , etc. in the reaction system makes it possible to form a uniform, reaction-produced transparent aqueous solution, and finally makes it possible to provide tin oxide having very good conductivity. Therefore, such coexistence is desirable.

20 Desirably, the quantity of such a dopant to be used should be determined to be in the range of from 0.01 to 0.35 mol, preferably from 0.03 to 0.25 mol, for one mol of tin carboxylate.

In this way, a transparent aqueous solution of the tin compound showing a pH below 1.5 can be obtained in a reaction time usually from 5 to 50 minutes. The aqueous solution without any treatment, or 25 after suitable concentration or addition of a dopant, can be subjected to shaping, such as formation of a membrane on a substrate such as a glass plate, or after being made into powder by a suitable operation such as spray drying, it can be calcinated to produce conductive tin oxide.

The calcination conditions employed are generally temperatures from 400°C to 1000°C, preferably from 500° to 800°C, for 0.5 to 5 hours, preferably for 1 to 3 hours.

30 As mentioned above, from the transparent aqueous tin compound solution of this invention, it is possible to form tin oxide of excellent transparency, uniformity, compactness, conductivity, etc. in any form such as powder, membrane, etc., without using any complicated apparatus or without any problem of inferior operability. These are the characteristic advantages of this invention.

Thus, the transparent aqueous tin compound solution and the tin oxide produced from said aqueous 35 solution are used in the use fields of fillers, paints, membranes, etc. for which conductivity is especially required, or in various use fields such as transparent heating elements, gas sensors, infrared reflexing membranes, lithium ion selective adsorption agents, catalysts, flame-retardants, etc.

Examples

40 The invention will be explained in detail by way of Examples in the following. In the Examples, the electrical resistance was obtained as follows:

The reaction-produced liquid is spray-dried and pulverized by means of a ball mill into particles having an average particle diameter of about 5 μ . The particles are calcinated at 500°C for 3 hours to produce a sample. One gram of the sample is packed into an electrode for solid matter use (SE-70 type), produced by 45 Ando Denki Co. Then the electrode spring is set, and by means of a LCR-meter (AX-221 type) produced by ADEX Co. Ltd., the electric resistance (Ω) is obtained.

The bulk density (g/ml) was obtained as follows:

50 A sample of 10 g is packed into a cell (inner diameter: 20.5 mm; length: 50 mm). The compressed heights (h mm) are obtained under various loads of the electrode piston (inner diameter: 20 mm, length: 60 mm).

The resistivity ($\Omega\cdot\text{cm}$) was obtained by measuring the electric resistance R (Ω) using a four probe ohm meter (3224 type) produced by Hioki Denki Co. Ltd.

Example 1

55 Stannous oxalate (SnC_2O_4) was added to water of room temperature and the mixture was stirred to form a slurry. An aqueous 35 weight % hydrogen peroxide solution was added to the slurry in the ratios shown in Table 1 below for one mol of SnC_2O_4 to react for 30 minutes, producing 5 kinds of transparent aqueous solutions (A—E). The concentration of SnC_2O_4 in each reaction system was determined at 15 weight %.

60 The pH value of each reaction-produced liquid as well as the bulk density and electrical resistance and of the calcined samples were measured. The results are shown together in Table 1.

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Table 1

Sample	H ₂ O ₂ (mol)	pH of the reaction- produced liquid	Calcinated sample	
			Bulk density (g/ml) *	Electrical Resistance (k Ω)
A	1.0	1.7	2.4	1,600
B	1.3	1.7	2.4	1,400
C	1.6	0.8	3.2	160
D	2.0	0.6	3.4	150
E	2.2	0.6	3.3	150

* Values under the load of 10^8 Pa (1 t/cm²)

From the above Table, it is clearly understood that by following this invention, it is possible to provide a transparent aqueous tin compound solution which can form tin oxide having high compactness and exhibiting excellent low electrical resistance.

On the other hand, to a 15 weight% aqueous solution of stannic chloride, an aqueous ammonium solution was added so that the pH of the solution became 8, thereby to produce colloidal stannic hydroxide. The colloidal stannic hydroxide was evaluated in the same way as above. The bulk density was 2.2 g/ml and the electrical resistance was 1,700 k Ω .

Example 2

Five kinds of transparent aqueous solutions (F—J) were produced in the same way as Example 1 (D) except that amounts of Sb₂O₃ shown in Table 2 below were added for one mol of SnC₂O₄. The values of the electrical resistance of these solutions were measured, and the results are shown in Table 2.

Table 2

Sample	F	G	H	I	J
Quantity of Sb ₂ O ₃ added (mol)	0.005	0.03	0.05	0.25	0.35
Electrical Resistance (Ω)	135	3	1	3	30

The electrical resistance of the dispersion liquid obtained by adding 0.1 mol Sb₂O₃ to Example 1 (D) was 12 k.

Example 3

Two kinds of transparent aqueous solutions (K and L) were produced by adding SnC₂O₄ to room temperature water and adding 1 mol or 2 mol of a 35 weight % aqueous H₂O₂ solution for 1 mol of SnC₂O₄ under stirring to react for 30 minutes.

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Transparent aqueous solutions (M and N) were produced in the same way as above except that one mol of Sb_2O_3 for 0.1 mol of SnC_2O_4 . The concentration of SnC_2O_4 in the reaction system was determined to be 15 weight % in each case.

After spray-drying the thus obtained aqueous solutions (K—N) the resulting solid matter was pulverized into particles of average particle diameter of about 5μ by means of a ball mill. The particles were then calcinated in air at 500°C for 3 hours, thus producing 4 kinds of tin oxide powder (K—N). The bulk density and resistivity were measured under a load of 10^8 Pa (1 t/cm^2). The results are shown in Table 3.

Table 3

Sample	Quantity added for 1 mol of SnC_2O_4		Bulk density (g/ml)	Resistivity ($\Omega\cdot\text{cm}$)
	H_2O_2 (mol)	Sb_2O_3 (mol)		
K	1	0	2.4	4×10^2
L	2	0	3.4	5×10^1
M	1	0.1	2.4	8×10^{-1}
N	2	0.1	3.4	7×10^{-2}

It is understood from the above Table that by determining the quantity of H_2O_2 within the range of this invention, it is possible to improve the conductivity, and by adding a dopant the conductivity is remarkably elevated.

Example 4

Under various loads, measurement of bulk density and resistivity was made on Example 3 sample N and tin oxide conductive powder T-1 produced by Mitsubishi Metal Co. Ltd. The results are shown in Table 4.

Table 4

Load (Pa (t/cm^2))		10^8 (1)	$2 \cdot 10^8$ (2)	$3 \cdot 10^8$ (3)	$4 \cdot 10^8$ (4)	$5 \cdot 10^8$ (5)
Bulk density (g/ml)	Sample N	3.4	3.8	4.0	4.2	4.3
	T-1	2.2	2.7	3.3	3.9	4.3
Resistivity ($\Omega\cdot\text{cm}$)	Sample N	7×10^{-2}	4×10^{-2}	3.4×10^{-2}	3.2×10^{-2}	3.0×10^{-2}
	T-1	8×10^{-1}	7.5×10^{-1}	7×10^{-1}	7×10^{-1}	7.0×10^{-4}

It is clearly understood from the above Table that the product of this invention has excellent conductivity under every load.

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Four kinds of tin oxide powder (O—R) were produced in the same way as Example 3 sample N except that the kind of dopant was varied.

The resistivity under the load of 10^8 Pa (1 t/cm^2) was measured for each sample. The results are shown in Table 5.

Table 5

Sample	Kind of dopant	Resistivity ($\Omega \cdot \text{cm}$)
O	SnF_2	11
P	$\text{Cu}(\text{HCOO})_2$	34
Q	Nb_2O_5	38
R	$\text{Ce}_2(\text{C}_2\text{O}_4)_3$	23
L	none	50

Example 6

Six kinds of tin oxide powder (S—X) were produced in the same way as Example 3 sample N except that the quantity of Sb_2O_3 was varied.

The values of resistivity of these samples under the load of 10^8 Pa (1 t/cm^2) are shown in Table 6.

Table 6

Sample	S	T	U	V	W	X
Quantity of Sb_2O_3 added (mol)	0.01	0.03	0.05	0.25	0.35	0.4
Resistivity ($\Omega \cdot \text{cm}$)	7×10^{-1}	1×10^{-1}	8×10^{-2}	5×10^1	2×10^2	3×10^3

Example 7

The transparent aqueous solution (N) of Example 3 was spinner coated at 3,000 rpm onto a quartz glass substrate and was calcinated in air at 700°C for two hours to produce a transparent conductive membrane. The properties of the membrane are shown in Table 7.

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Table 7

5	Membrane thickness	Percent transmittance	Surface resistivity	Membrane surface
10	(mm (Å))	(%)	(Ω / \square)	
15	30 (300)	90	200	smooth uniform

Claims

1. A transparent aqueous tin compound solution obtained by reacting a tin carboxylate with hydrogen peroxide in the molar ratio of 1:1.5 or above in an aqueous medium.
2. The transparent aqueous solution as claimed in Claim 1 obtained by making coexist in the reaction system, a dopant of a quantity of from 0.01 to 0.35 mol for one mol of the tin carboxylate.
3. A method of producing a transparent conductive tin oxide characterized by reacting a tin carboxylate with hydrogen peroxide in the molar ratio 1:1.5 or above in an aqueous medium, and calcinating the thus-obtained transparent aqueous solution at a temperature above 400°C.
4. The method as claimed in Claim 3 wherein a dopant is made to coexist in the reaction system in the ratio of from 0.01 to 0.35 mol for one mol of the tin carboxylate.

Patentansprüche

1. Transparente wäßrige Lösung einer Zinnverbindung, erhalten durch Umsetzung eines Zinn-carboxylats mit Wasserstoffperoxid in einem Molverhältnis von 1:1,5 oder darüber in einem wäßrigen Medium.
2. Transparente wäßrige Lösung nach Anspruch 1, erhalten in der Weise, daß man in dem Reaktionssystem ein Dotierungsmittel in einer Menge von 0,01 bis 0,35 Mol pro 1 Mol des Zinn-carboxylats vorliegen läßt.
3. Verfahren zur Herstellung eines transparenten leitenden Zinnoxids, gekennzeichnet durch Umsetzung eines Zinn-carboxylats mit Wasserstoffperoxid in einem Molverhältnis 1:1,5, oder darüber in einem wäßrigen Medium und Kalzinieren der auf diese Weise erhaltenen transparenten wäßrigen Lösung bei einer Temperatur oberhalb 400°C.
4. Verfahren nach Anspruch 3, wobei man ein Dotierungsmittel in dem Reaktionssystem in einem Verhältnis von 0,01 bis 0,35 Mol pro 1 Mol des Zinn-carboxylats vorliegen läßt.

Revendications

1. Solution aqueous transparente d'un composé d'étain, obtenue par réaction d'un carboxylate d'étain avec le peroxyde d'hydrogène en un rapport molaire égal ou supérieur à 1:1,5 dans un milieu aqueux.
2. Solution aqueous transparente suivant la revendication 1, obtenue en faisant coexister dans le mélange réactionnel un dopant en une quantité de 0,01 à 0,35 mole pour une mole du carboxylate d'étain.
3. Procédé de production d'un oxyde d'étain conducteur transparent, caractérisé en ce qu'il consiste à faire réagir un carboxylate d'étain avec le peroxyde d'hydrogène en un rapport molaire égal ou supérieur à 1:1,5 dans un milieu aqueux, et à calciner la solution aqueuse transparente ainsi obtenue à une température supérieure à 400°C.
4. Procédé suivant la revendication 3, dans lequel on fait coexister dans le mélange réactionnel un dopant en un rapport de 0,01 à 0,35 mole pour une mole du carboxylate d'étain.

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